Physics. — *"On the critical density for associating substances."*
By Prof. J. D. van der Waals.

(Communicated in the meeting of March 28, 1914)

For non-associating substances the critical density is determined by the relation:

$$D_k = 0{,}001293 \frac{M}{28{,}84} \frac{p_k}{RT_k} s.$$

We then understand by density the number of grams that 1 cm³ weighs, by M the molecular weight, and by s the factor introduced by Sydney Young, which denotes how many times the critical volume is smaller than would be the case if the substance should have followed the laws of Boyle and Gay-Lussac. So that s corresponds to the relation:

$$s \frac{p_k \, v_k}{RT_k} = \frac{p_0 v_0}{RT_0}$$

or as $p_0 = 1$ and $RT_0 = 1$, to:

$$s \frac{p_k v_k}{RT_k} = v_0 .$$

If we imagine a quantity of substance present equal to M, then $v_0 = \dfrac{28{,}84}{0{,}001293} = 22305$, and the given equation for D_k becomes duly:

$$D_k = \frac{M}{v_k} .$$

The determination of v_k is therefore sufficient for the determination of D_k, and also, when T_k and p_k are taken into account, for the determination of the quantity s. We owe it chiefly to Sydney Young that the value of D_k and the corresponding value of s is known for a great number of substances. If the observations do not allow the direct determination of v_k, one may avail oneself of other methods to determine D_k for the calculation of s, but not with the same certainty, and determine the quantity s by the aid of this value and the knowledge of M, p_k, and T_k according to the above given formula. Now it is remarkable to how high a degree this quantity is found -the same for alle non-associating substances, and how little it appears to differ from 3,77. Whether it really has this value for all normal substances, whether a smaller value will exist particularly for substances with small molecules, I will not discuss again at

present, but I will point out that the appreciably larger values of s, which are given for associating substances by SYDNEY YOUNG, may be perfectly accounted for with this value of $s = 3,77$.

SYDNEY YOUNG (Proceedings Physical Society of Londen July 1894) gives $s = 5$ for acetic acid, $s = 4,52$ for methyl alcohol, $s = 4,02$ for ethyl alcohol, etc.

For associating substances a modification must be applied in the formula for D_k, which we have given above, namely in the value of M. Let there be present $1 - x_k$ single molecules, and x_k double molecules, then the molecular weight present in the critical state $= M_1 (1 - x_k) + M_2 x_k$ and M_2 being $= 2M_1$, the molecular weight $= M_1 (1 + x_k)$. Hence we get:

$$D_k = \frac{0,001293}{28,84} M_1 (1 + x_k) \frac{p_k}{RT_k} s$$

which, if

$$\frac{p_k v_k}{RT_k} s = v_0$$

is put again, agrees with:

$$D_k = \frac{M}{v_k} = \frac{M_1 (1 + x_k)}{v_k}.$$

The ratio between the critical density and that which would be found when the laws of BOYLE GAY-LUSSAC were followed, is therefore greater for two reasons. First because of the existence of the quantity x_k, and secondly on account of the existence of $s > 1$. And SYDNEY YOUNG's value for acetic acid, viz. 5, is the product $s (1 + x_k)$. And assuming again 3.77 for s, we determine $1 + x_k = \frac{5}{3.77}$ or $1 + x_k = 1,324$. But we are only sure of this value of x_k, if we may assume $s = 3,77$ also in this case. And though this is probable, à priori, because the value of s, deviating from $\frac{8}{3}$, the value obtained when b is put invariable, only depends on the way in which b decreases, yet it seemed desirable to me to investigate this more closely. For this purpose I have examined the equation of state for an associating substance more accurately. It has the form:

$$p = \frac{RT}{v - b_k} - \frac{a_x}{v^2}.$$

The numerator, which would be equal to $R_1 TM_1 (1 - x) + R_2 TM_2 x$ may be written in this simple form, because $M_1 R_1 T = M_2 R_2 T$.

The value of b_x is $b_1(1-x) + b_2x$, or as $b_2 = 2b_1$, we find the value $b_1(1+x)$ for b_x. And the value of a_x consists of 3 terms, viz. 1. $a_1(1-x)^2$, the contribution yielded by the single molecules present. 2. $2 \times 2a_1x(1-x)$, the attraction of the single molecules present exerted on the present double molecules and vice versa, and 3. the term. $(2a_1x)^2$. Joining these we find:

$$a_1(1-x+2x)^2 = a_1(1+x)^2.$$

We can then reduce the equation of state to the following form:

$$p = \frac{\dfrac{RT}{1+x}}{\dfrac{v}{1+x} - b_1} - \frac{a_1}{\left(\dfrac{v}{1+x}\right)^2}.$$

When we compare this shape of the equation of state of the associating substance with that of the substance, when it would contain only single molecules, we see, that with given pressure and temperature $\dfrac{T}{1+x} = T_1$, a volume V_x of the associating substance corresponds to a volume V_1 of the single molecules, which volume V_x is $(1+x)$ times larger, and that over the entire region. Only the value of x is variable. And as I may suppose known, another equation, viz. $\left(\dfrac{d\psi}{dx}\right)_v = 0$ is required for the determination of x. But at the moment we do not require the knowledge of the course of x.

A quantity M_1 of a substance, consisting only of single molecules, is in a volume v_1, and a quantity $M_1(1+x)$ of an associating substance is in a volume $v_1(1+x)$. The density is therefore the same for given p and $\dfrac{T}{1+x}$ in these cases. I had expected this result, and even pronounced it, though I may only consider this thesis as proved by the foregoing.

Before proceeding further in the investigation of the value of s for the associating substance, I will point out some particularities about the critical circumstances. We find for $(RT_k)_x$ by approximation:

$$(RT_k)_x = \frac{8}{27} \frac{a_1(1+x_k)^2}{(b_1)_k(1+x_k)} = \frac{8}{27} \frac{a_1}{(b_1)_k}(1+x_k),$$

and for $(p_k)_x$:

$$(p_k)_x = \frac{1}{27} \frac{a_1(1+x_k)^2}{(b_1)_k(1+x_k)^2} = \frac{1}{27} \frac{a_1}{(b_1)_k^2},$$

and for $\dfrac{(RT_k)_x}{(p_k)_x}$ the value $8(b_1)_k(1+x_k)$, and as $(b_1)_k$ is smaller than $(b_1)_g$, about:

$$\frac{(RT_k)_x}{(p_k)_x} = 7\,(b_1)_g\,(1+x_k) = \frac{RT_{k_1}}{p_{k_1}}\,(1+x_k)$$

For the quantity $\dfrac{T_k}{p_k}$ we find (see my preceding communication p. 889, These Proc. Feb. 1914) the value of 10,415 much too large for $\dfrac{T_{k_1}}{p_{k_1}}$. Also by comparison of these values $(1+x_k)$ might be determined, but with less certainty.

The critical temperature of an associating substance is therefore greater than might be inferred from the molecular size of the single molecule — but the critical pressure has not changed.

Let us now return to the determination of $\dfrac{pv}{T}$ for the critical circumstances of the associating substance, and compare this with $\dfrac{pv}{T}$ for the critical circumstances for permanent single molecules. For the associating substance this value is equal to $\left(\dfrac{p_k v_k}{T_k}\right)_x$. If we replace the value of (v_k) by $(1 + x)\,v_1$ for $(p_k)x$ and $(T_k)_x$, we have to determine the value of $\dfrac{(T_k)_x}{(p_k)_x}\,v_1\,(1 + x_j)$, and if we now substitute (p_{k_1}) for $(p_k)_x$, and $(T_{k_1})\,(1 + x)$ for $(T_k)_x$, the required value becomes equal to:

$$\frac{(p_k)_1\,v_1}{(T_k)_1}.$$

And now we have still to show that $v_1 = (v_k)_1$.

If b is variable, the critical volume is, indeed, not $3b_g$, but $l\,b_g$, in which l is somewhat smaller than 2, or $l'\,b_k$, when l' is somewhat greater than 2, so that $(v_k)_x = l\,b_g\,(1+x_k)$. On the supposition that l has the same value for all substances, at least for substances with not too small a number of atoms in the molecule, we have shown by this that

$$\left(\frac{p_k v_k}{T_k}\right)_x = \left(\frac{p_k v_k}{T_k}\right)_1$$

and that therefore the quantity s may be put equal to 3,77 also for the associating substance.

The foregoing considerations are not confined to cases in which real association exists, but may also be applied to cases in which what I have called quasi association is found. This probably occurs already to an appreciable degree in the critical circumstances for alcohols. In case of real association there are double and triple

molecules present, the possibility of the existence of which chemistry must be able to show by means of the construction of the molecule; in case of quasi-association, however, there are local accumulations of molecules, which may lead to the question if the cause why they occur in a greater degree for one substance than for another, may perhaps be found in the form of the molecules. But this question cannot be answered with any certainty yet. Nor can the question be answered as yet for real association why for acetic acid and for aldehydes and perhaps some other substances as nitriles, this association exists

The degree of aggregation for the quasi-association will probably not be the same for each of these aggregations, but to simplify the calculation we may assume on an average the value n for it, which I estimated already before at 8 or 9. It is, however, to be expected that also the mean value n will vary with pressure and temperature. But since we have only to examine the influence of the quasi association on the critical circumstances here, we may confine ourselves to an invariable value of n. Proceeding here as we did above, we find for $1 - x$ non aggregated molecules, and x aggregations the molecular weight equal to $M_1 (1 - x + nx)$. For b_k we find $b_1 (1 - x + nx)$ and for a_k the value $a_1 \{1 - x + nx\}_2$.

And we may write the equation of state:

$$ p = \frac{\dfrac{RT}{1+(n-1)x}}{\dfrac{v}{1+(n-1)x} - b_1} - \frac{a_1}{\left[\dfrac{v}{1+(n-1)x}\right]^2} . $$

Hence with given pressure and temperature $\dfrac{T}{1+(n-1)x} = T_1$ is

$\dfrac{v_k}{1+(n-1)x} = v_1$, if we should call v_1 the volume which the substance would occupy at the same pressure and corresponding temperature, when it were not in quasi-association. The value of $v = v_1 (1+(n-1)x)$.

In the first case the density is equal to $\dfrac{M_1}{v_1}$ in the second to $\dfrac{M_1(1+(n-1)x)}{v}$, so of the same value. Thus we shall also find:

$$ D_k = \frac{0,001293}{28.84} M_1 [1+(n-1)x_k] \frac{(p_k)_x}{(RT_k)_x} $$

$$ (T_k)_x = (T_k)_1 [1+(n-1)x_k] $$

$$ (p_k)_x = (p_k)_1 $$

and

$$ (V_k)_x = (v_k)_1 [1+(n-1)x_k] $$

And so also:

$$\left(\frac{p_k v_k}{T_k}\right)_x = \left(\frac{p_k v_k}{T_k}\right)_1$$

According to the values given by SYDNEY YOUNG $s[1+(n-1)v_k$ has the value 4,52 for methyl alcohol, 4,02 for ethyl alcohol, and also 4,02 for propyl alcohol. With $s = 3.77$ we found for:

Methyl alcohol $1 + (n-1)x_k = 1,2$
Ethyl alcohol $1 + (n-1)x_k = 1,0663$
Propyl alcohol $1 + (n-1)x_k = 1.0663$

Now for these three substances $\left(\dfrac{T_k}{p_l}\right)_x$ is respectively equal to:

6,52, 8,2 and 10,7.

By the aid of the value of $1 + (n-1)x_k$ for these three substances we calculate $\left(\dfrac{T_k}{p_k}\right)$ or b_1, and then we find:

5,43, 7,69 and 10,03

The differences are almost equal, viz. 2.26 and 2.34, but they are smaller than what we have found for CH_2 in the series of the saturated hydrocarbons, and this seems inexplicable for the time being. Unless we might assume that an atom C, when bound to O, is smaller than when it is bound to H, and that besides it could also impart this property to other atoms C to which it is bound. The value for ethyl alcohol calculated here is, however, in perfect agreement with the value for ether calculated in the preceding communication. With b for ether equal to 13,12 follows the value 7.60 for alcohol by subtraction of 2×2.76. For methyl ether, for which we found $b = 7.55$ before, we could now find 5.43, by putting $CH_2 = 2.12$. But this is possible, when C bound to O should be smaller than C bound to C. The difference, however, is then greater than could be expected. So that we are again confronted with the question whether in case of quasi-association circumstances occur which we have not yet duly taken into account in our discussion. This, however, is quite beside the subject of this communication which purposes to show that we may consider the quantity s as entirely, or almost entirely of the same value at least for polyatomic molecules. The slight differences are then entirely subject to the relation given by me before $\dfrac{s^2}{f-1} = \dfrac{64}{27}$, which, however, only holds unmodified for normal substances; the value of s for associating substances has been discussed here, and a closer investigation about the value of f for such substances would also be desirable.